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PENTAMETHYL-CYCLOPENTADIENYL-SUBSTITUTED SILICON COMPOUNDS. (U)

MAY 82 A H COWLEY, E A EBSWORTH, S MEHROTRA

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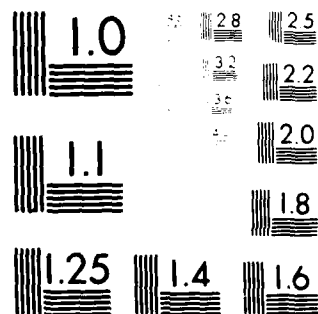
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## PENTAMETHYLCYCLOPENTADIENYL-SUBSTITUTED SILICON COMPOUNDS

A. H. Cowley,<sup>a</sup> E. A. V. Ebsworth,<sup>b</sup> S. K. Mehrotra,<sup>a</sup> D. W. H. Rankin,<sup>b</sup>  
and M. D. Walkinshaw<sup>b</sup>

<sup>a</sup>Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, U.S.A.

<sup>b</sup>Department of Chemistry, University of Edinburgh, Edinburgh, EH9 3JJ, U.K.

The syntheses of the first pentamethylcyclopentadienyl compounds of silicon are described; the structure of ( $\eta^1\text{-Me}_5\text{C}_5$ )SiCl<sub>3</sub> has been determined by X-ray crystallography.

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Pentamethylcyclopentadienyl compounds of the main-group elements are of interest because their structures and properties often differ significantly from those of the corresponding cyclopentadienyl derivatives. Amongst the Group IVA elements, Me<sub>5</sub>C<sub>5</sub> compounds have been reported for Ge,<sup>1,2</sup> Sn,<sup>1,2,3</sup> and Pb,<sup>4</sup> but not for Si. We report (i) the syntheses of (Me<sub>5</sub>C<sub>5</sub>)SiCl<sub>3</sub> (1) and (Me<sub>5</sub>C<sub>5</sub>)SiHCl<sub>2</sub> (2), (ii) metathesis reactions of (2), and (iii) the X-ray crystal structure of (1), to our knowledge the first such data for a mono-hapto Me<sub>5</sub>C<sub>5</sub> compound.

Pentamethylcyclopentadienyltrichlorosilane (1) was prepared in 40% yield by the slow addition of SiCl<sub>4</sub> (63.9 mmol) to a solution of Me<sub>5</sub>C<sub>5</sub>Li (63.9 mmol) in 400 mL of Et<sub>2</sub>O. Filtration of the reaction mixture, followed by the evaporation of solvent left a colourless oil, b.p. 60°C/0.05 torr, which crystallised upon standing at room temperature. Compound 1 was characterised by elemental analysis, mass spectroscopy [ $m/e$  269 ( $M^+$ )] and

n.m.r. spectroscopy;  $^1\text{H}$  n.m.r. ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  1.78 (s);  $^{13}\text{C}$  n.m.r. ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  12.57 p.p.m. (s,  $\text{Me}_5\text{C}_5$ ). Interestingly, (1) can be handled in air for short periods of time; moreover all the compounds described herein exhibit long-term stability at ambient temperature. The latter observation provides an interesting contrast with  $\text{C}_5\text{H}_5$  compounds of silicon which are not stable under these conditions.<sup>1,5</sup> An X-ray crystal structure of (1) was undertaken to elucidate the environment of the  $\text{SiCl}_3$  moiety.

Crystal data:  $\text{C}_{10}\text{H}_{15}\text{Cl}_3\text{Si}$ ,  $M = 269.71$ , orthorhombic, space group  $\text{Pnam}$ ,  $a = 8.284(3)$ ,  $b = 12.645(1)$ ,  $c = 12.836(2)$  Å,  $U = 1345$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.33$  g cm<sup>-3</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.71069$  Å,  $\mu(\text{Mo-K}\alpha) = 7.3$  cm<sup>-1</sup>. The structure was solved by direct methods. Full-matrix least-squares refinement using 1212 observed reflections yielded a conventional  $R$  value of 0.048.<sup>†</sup>

The  $\text{Me}_5\text{C}_5$  ring of (1), which is essentially planar,<sup>†</sup> is attached to Si in the monohapto manner (Figure 1). The n.m.r. spectral equivalence of the ring Me groups must therefore arise from circumannular migration of the  $\text{SiCl}_3$  group. The Si-C bond length of 1.867(3) Å is quite normal;<sup>6</sup> however, the steric demands of the  $\text{Me}_5\text{C}_5$  ring are evident from the fact that the Cl-Si-Cl bond angles of the  $\text{SiCl}_3$  moiety are 2-5° less than the tetrahedral angle.

The dichlorosilane ( $\text{Me}_5\text{C}_5$ ) $\text{SiHCl}_2$  (2) (b.p. 50°C/0.05 torr) was prepared in 60% yield by the action of  $\text{Me}_5\text{C}_5\text{Li}$  on  $\text{SiHCl}_3$  as described above for (1). The structure assignment for (2) follows from spectroscopic data: mass spectrum [ $m/e$  235 ( $M^+$ )];  $^1\text{H}$  n.m.r. ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  1.82 (s, 15H,  $\text{Me}_5\text{C}_5$ ) and 4.05 (s, 1H, SiH);  $^{13}\text{C}$  n.m.r. ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  11.76 (s,  $\text{Me}_5\text{C}_5$ ), 121.92 (s,  $\text{Me}_5\text{C}_5$ ).

As in the case of the bulky  $(\text{Me}_3\text{Si})_3\text{C}$  substituent,<sup>7</sup> replacement of one Si-Cl by a Si-H bond facilitates nucleophilic substitution at silicon. Thus,

whereas (1) reacts incompletely with excess  $\text{Me}_2\text{NH}$  or  $\text{MeOH/Et}_3\text{N}$  in n-hexane solution, (2) reacts readily under these conditions to produce virtually quantitative yields of  $(\text{Me}_5\text{C}_5)\text{SiH}(\text{NMe}_2)_2$  (3) and  $(\text{Me}_5\text{C}_5)\text{SiH}(\text{OMe})_2$  (4). Compounds (3) and (4) were characterised by elemental analysis and spectroscopy: (3) [b.p.  $53-56^\circ\text{C}/0.05$  torr,  $\underline{m/e}$  252 ( $\underline{M}^+$ )]; (4) [b.p.  $46-48^\circ\text{C}/0.05$  torr,  $\underline{m/e}$  226 ( $\underline{M}^+$ )].  $^1\text{H}$  n.m.r. (3) ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  1.78 (s, 15H,  $\text{Me}_5\text{C}_5$ ),  $\delta$  2.36 (s, 12H,  $\text{Me}_2\text{N}$ ),  $\delta$  4.24 (s, 1H, SiH); (4) ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  1.92 (s, 15H,  $\text{Me}_5\text{C}_5$ ),  $\delta$  2.62 (s, 6H, OMe);  $^{13}\text{C}$  n.m.r. (3) ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  11.90 (s,  $\text{Me}_5\text{C}_5$ ),  $\delta$  38.69 (s,  $\text{Me}_2\text{N}$ ); (4)  $\delta$  11.98 (s,  $\text{Me}_5\text{C}_5$ ),  $\delta$  51.85 (s, MeO).

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## REFERENCES

- 1 A. Davison and P. E. Rakita, Inorg. Chem., 1970, **9**, 289.
- 2 P. Jutzi, F. Kohl, P. Hofmann, C. Krüger, and Y.-H. Tsay, Chem. Ber., 1980, **113**, 757.
- 3 P. Jutzi and F. Kohl, J. Organomet. Chem., 1979, **164**, 141.
- 4 J. L. Atwood, W. E. Hunter, A. H. Cowley, R. A. Jones, and C. A. Stewart, Chem. Comm., 1981, 925.
- 5 H. Gilman and L. A. Gist, Jr., J. Org. Chem., 1957, **22**, 250; H. P. Fritz and C. G. Kreiter, J. Organomet. Chem., 1965, **4**, 313.
- 6 Chem. Soc. Spec. Publ. No. 18 (1965) S 22s.
- 7 S. S. Dua, C. Eaborn, D. A. R. Happer, S. P. Hopper, K. D. Safa, and D. R. M. Walton, J. Organomet. Chem., 1979, **178**, 75.

#### FOOTNOTES

† The atomic co-ordinates for this work are available upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation of this communication.

‡ The average root mean square deviation from the best plane is 0.007 Å.

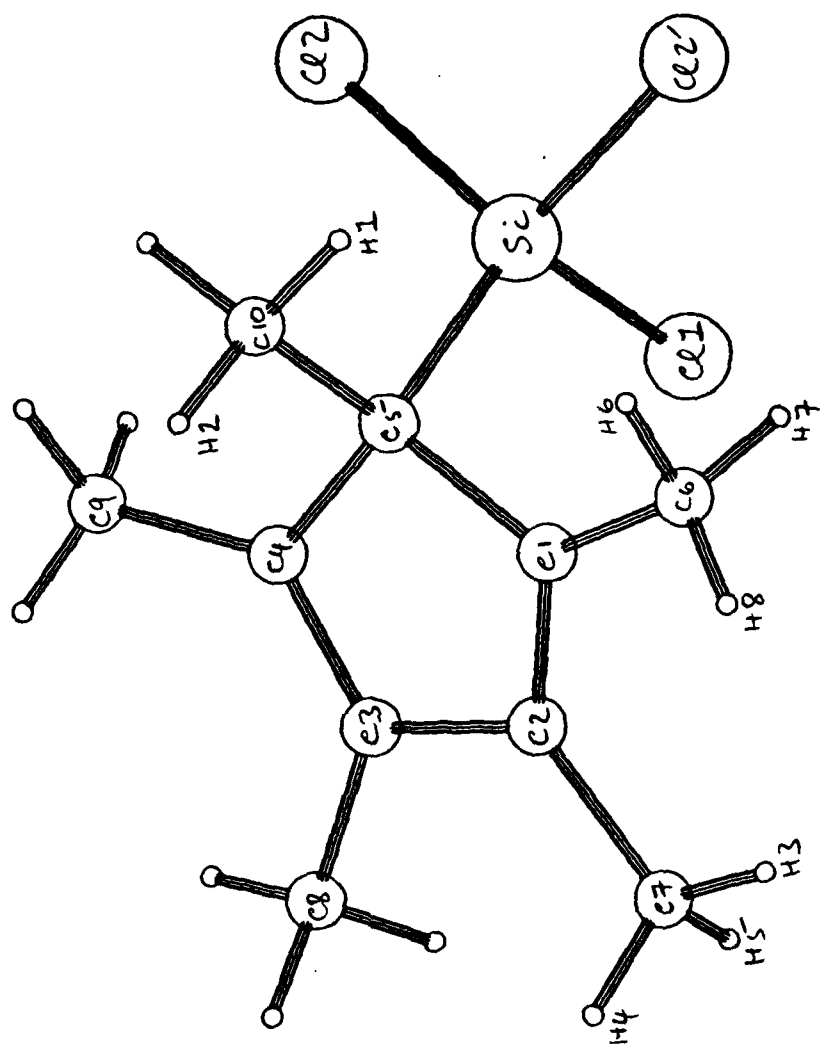


FIGURE CAPTIONS

FIGURE 1. Molecular structure of  $(\eta^1\text{-Me}_5\text{C}_5)\text{SiCl}_3$  (1). The molecule possesses a plane of symmetry passing through Cl(1), Si, C(5), C(10), and H(2) and bisecting the C(2)-C(3) bond. Important bond lengths are Si - C(5) 1.867(3), Si - Cl(1) 2.011(1), Si - Cl(2) 2.036(1) Å. Important bond angles are C(5)-Si-Cl(1) 112.5 (1), C(5)-Si-Cl(2) 112.2(1), Cl(1)-Si-Cl(2) 107.5(1), and Cl(2)-Si-Cl(2') 104.4(1)°.



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